Kinetic, Thermodynamic and Isotherm Studies on the Removal of Methylene Blue Dye using Acid Activated Glossocardia linearifolia Stem

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Abstract: *The research of the present work was to investigate the removal of methylene blue dyes from aqueous solution by using Acid Activated Glossocardia linearifolia Stem (AGLS) carbon. Generally, dyes are organic compounds used as colouring products in chemical, textile, paper, printing, leather, plastics and various food industries. Contaminated waste water passed out from the industry should be treated. In this study, Glossocardia linearifolia Stem carbon was studied for its potential use as an adsorbent for removal of a cationic dye methylene blue. The various factors affecting adsorption, such as initial dye concentration, contact time, adsorbent dose and effect of temperature, were evaluated. The experimental data were fitted into the pseudo-second order kinetic model. The equilibrium of adsorption was modeled by using the Langmuir and Freundlich isotherm models. The result obtained in the present work suggests the AGLS may be utilized as a low cost adsorbent for methylene blue dye removal from aqueous solution.*
Key Words: *Acid activated Glossocardia linearifolia Stem (AGLS); methylene blue; adsorption isotherm; kinetics; equilibrium models.*

I. Introduction

Dyes are widely used, generally in the textiles, plastics, paper, leather, food industry to color products. In the process of washing and finishing coloured products, waste water contaminated with dyes is generated. The contaminated waste waters are hazardous, which is a great threat to environment [1-3]. Dye contamination in wastewater causes problems in various ways: the presence of dyes in water, even in very low quantities, is highly visible and undesirable; color interferes with penetration of sunlight into waters; retards photosynthesis; inhibits the growth of aquatic biota and interferes with gas solubility in water bodies. These materials are the complicated organic compounds and they resist against light, washing and microbial invasions [4-7]. The need for the treatment of dye contaminated waste water arose from the environmental impact [8]. Activated minerals are one of the most popular adsorbents used for the removal of toxic substances from waste water. This could be related to their extended surface area [9]. In recent years it has been increasingly used for the prevention of environmental pollution and antipollution laws have increased the sales of low-cost activated minerals for control the of air and water pollution. Various techniques like precipitation, ion exchange, chemical oxidation and adsorption have been used for the removal of toxic pollutant from, wastewater. Methylene blue (MB) is selected as a model compound for evaluating the potential of AGLS to remove dye from aqueous solution.

II. Materials And Methods

2.1 Adsorption studies

Methylene blue (MB) was employed for the adsorbate in the adsorption experiments. Adsorption from the liquid phase was carried out to verify the nature, the porosity and the capacities of the samples. An aqueous solution with a concentration of 25-125 mg/L was prepared by mixing an appropriate amount of MB with distilled water. Adsorption experiments were conducted by placing 0.025 g of the AGLS samples and 50 ml of the aqueous solution in a 250 ml of glass-stoppered flask. The flask was then put in a constant-temperature shaker bath with a shaker speed of 150 rpm. The isothermal adsorption experiments were performed at 30 ±2°C.
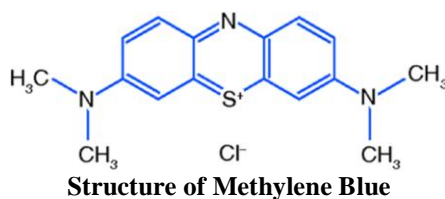
2.2 Preparation of adsorbent materials

Glossocardia linearifolia

The Glossocardia linearifolia Stem collected from agricultural area was carbonized with concentrated Sulphuric acid and washed with water and activated around 600°C in a muffle furnace for 5 hrs. Then it was taken out, ground well to fine powder, sieved and stored in vacuum desiccators.

2.3 Preparation of adsorbate

Methylene blue was chosen in this work because of its strong adsorption onto solids and its recognized usefulness in characterizing adsorptive material. Methylene blue is employed to evaluate the adsorption characteristics of carbon. A known weight of 1000 mg of MB was dissolved in about one litre of distilled water to get the stock solution.

Structure of Methylene Blue

2.4 Batch equilibrium method

The adsorption experiments were carried out in a batch process at 30, 40, 50 and 60° C. A known weight of AGLS was added to 50 ml of the dye solutions with an initial concentration of 25 mg/L to 125 mg/L, which is prepared from 1000 mg/L of methylene blue stock solution. The contents were shaken thoroughly using a mechanical shaker with a speed of 150 rpm. The solution was then filtered at specific time intervals and the residual dye concentration was measured.

III. Results And Discussions

3.1 Characteristics of the adsorbent

Acid activated Glossocardia linearifolia stem is an effective adsorbent for the abatement of many pollutant compounds (organic, inorganic, and biological) of concern in water and wastewater treatment. Most of the solid adsorbents possess micro porous fine structure, high adsorption capacity, high surface area and high degree of surface, which consists of pores of different sizes and shapes. The wide usefulness of AGLS is a result of their specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determines the sorption activity. The physico-chemical properties of the chosen adsorbent are listed in Table 1.

Table 1. Equilibrium parameters for adsorption of mb dye onto AGLS adsorbent

M_0	Ce (Mg / L)				Qe (Mg / g)				Removal (%)			
	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C
25	1.45	1.26	1.03	1.09	47.09	47.47	47.92	47.81	94.18	94.94	95.84	95.62
50	5.28	4.84	3.21	3.00	89.43	90.30	93.56	93.98	89.43	90.30	93.56	93.98
75	11.63	10.35	10.00	9.07	126.7	129.28	129.98	131.84	84.48	86.18	86.65	87.89
100	25.76	23.26	10.00	19.62	148.4	153.46	179.98	160.75	74.23	76.73	89.99	80.37
125	41.87	37.76	21.76	30.76	166.2	174.46	206.47	188.47	66.50	69.78	82.58	75.38

Table 1-Characteristics of the Adsorbent

Properties	AGLS
Particle size(mm)	0.010
Density (g/cc)	0.1935
Moisture content (%)	0.1784
Loss in ignition (%)	0.010
pH of aqueous solution	5.2

3.2 Effect of contact time and initial dye concentration

The effect of contact time on the amount of dye adsorbed was investigated at 1000 mg/L concentration of the dye and the results are shown in Fig. 1. It is observed that the percentage removal of dye increases rapidly with an increase in contact time initially, and thereafter, beyond a contact time of about 45 min, no noticeable change in the percentage removal is observed. The percentage removals after 45 min were 85%. Therefore, the optimum contact time is considered to be 45 min. this is also the equilibrium time of the batch adsorption experiments, since beyond a contact time of 45 min, adsorption is not changed. The rapid removal of dye is observed at the beginning of the contact time is due to the percentage of large number of binding sites available for adsorption. The experimental results of adsorptions at different concentrations (25 to 125mg/L) are collected in Table 2. It is observed that percent adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of AGLS increased leads to increase in dye concentration. This means that the adsorption is highly dependent on initial concentration of dye. At lower concentration, the ratio of the initial number of dye molecules to the available surface area is low. Subsequently, the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption become less and hence the percentage removal of dye is dependent upon initial concentration [10, 11].
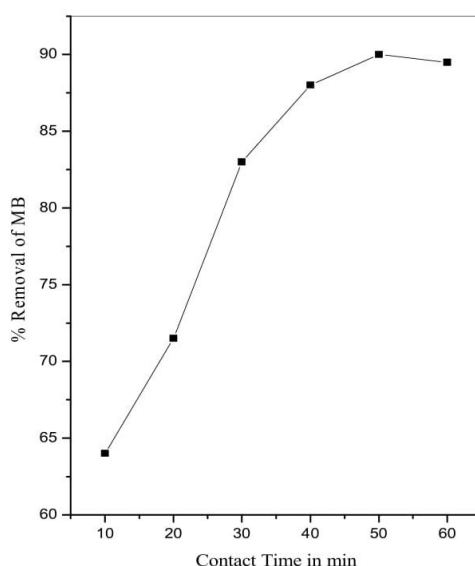

Fig: 1 Effect of Contact Time on the removal of MB dye [MB]=50mg/L; Temperature 30°C;
Adsorbent dose = 25 mg/50ml

Table 2. Langmuir and freundlich isotherm parameter for adsorption of mb onto AGLS

TEMP. (°C)	LANGUMUIR PARAMETERS		FRUENDLICH PARAMETERS	
	Q_m	b	K_f	N
30°	183.88	0.19	5.20	2.66
40°	193.91	0.20	5.31	2.60
50°	249.85	0.18	5.45	2.08
60°	207.88	0.23	5.58	2.56

3.3 Effect of adsorbent dosage

The adsorption of the methylene blue dye on AGLS was studied by varying the adsorbent dose (25–125 mg/50ml) for 50 mg/L of dye concentration. The percentage of adsorption increased with increases in the AGLS concentration, which is attributed to increased carbon surface area and the availability of more adsorption sites [12, 13]. Hence, all studies were carried out with 0.025g of adsorbent /50 ml of the varying adsorbate solutions.25, 50, 75, 100 and 125. The results obtained from this study are shown in Fig. 2. The amount of MB

adsorbed per gram reduced with increase in the dosage of AGLS. This reveals that the direct and equilibrium capacities of MB are functions of the activated AGLS dosage.
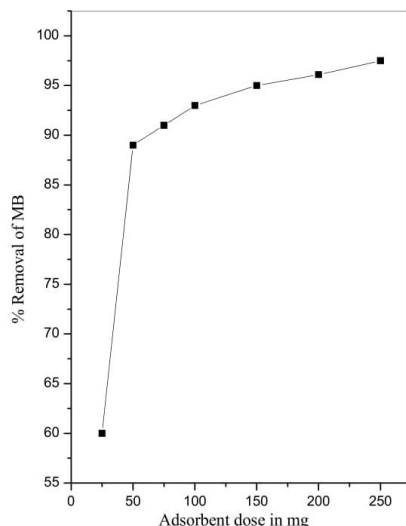

Fig: 2 Effect of Adsorbent does on the removal of MB dye [MB] =50mg/L; Contact Time 50 min;
Temperature 30°C

3.4 Effect of solution pH

The solution pH is one of the most important factors that control the adsorption of dye on the sorbent material. The adsorption capacity can be attributed to the chemical form of dye in the solution at specific pH. In addition, due to different functional groups on the adsorbent surface, which become active sites for the dye binding at a specific pH the effect of adsorption can vary substantially. Therefore, an increase in pH may cause an increase or decrease in the adsorption, resulting different optimum pH values dependent on the type of adsorbent. To examine the effect of pH on the % removal of MB dye , the solution pH were varied from 2.0 to 10.0 by adding acid or base to the stock solution. At high pH values the increases in adsorption may be due to the presence of negative charge on the surface of the adsorbent AGLS, that may be responded for the dye binding. However, as the pH is lowered, the hydrogen ions compete with dye for the adsorption sites in the adsorbent AGLS, the overall surface charge on the particles become positive and hinds the binding of positively charged dye. On other hand, decrease in the adsorption under pH >6.3 may be due to occupation of the adsorption sites by OH$^-$ ions which retard the approach of such dye further towards the adsorbent AGLS surface. From the experimental results, the optimum pH range for the adsorption of the MB dye is 2.0 to 6.5. The results are shown in Fig.3.
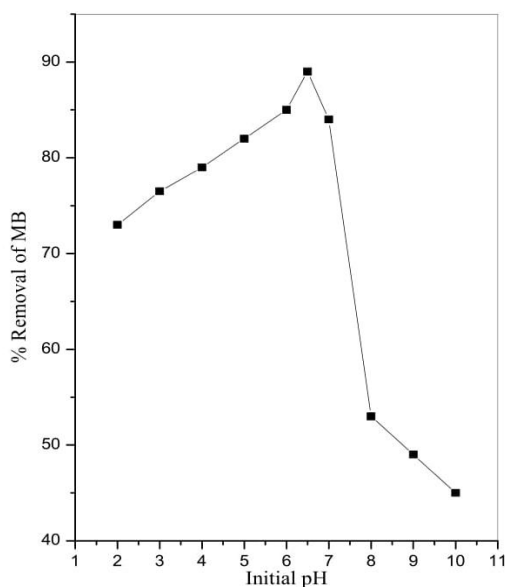

Fig: 3 Effect of initial pH on the removal of MB dye [MB] =50mg/L; Temperature 30°C;
Adsorbent dose = 25 mg/50ml

3.5. Adsorption isotherms
3.5.1 Langmuir isotherm

The theoretical Langmuir isotherm is used for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Therefore, the Langmuir isotherm model was chosen for the estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir non-linear equation is commonly expressed as follows:

$$C_{eq}/Q_{eq} = 1/Q_m b + C_{eq}/Q_m \quad \text{.....................} \text{(1)}$$

Where C_{eq} is the equilibrium concentration of adsorbate in the solution (mg/L), Q_{eq} is the amount adsorbed at equilibrium (mg/g), Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of C_{eq}/Q_{eq} vs. C_{eq} suggest the applicability of the Langmuir isotherms. The values of Q_m and b were calculated from slope and intercepts of the plots are given in Table 3.

Table 3. Dimensionless seperation factor (R_L) for adsorption of mb onto AGLS

(Cᵢ)	TEMPERATURE °C			
	30°C	40°C	50°C	60°C
25	0.17	0.16	0.17	0.14
50	0.09	0.09	0.09	0.07
75	0.06	0.06	0.06	0.05
100	0.04	0.04	0.05	0.04
125	0.03	0.03	0.04	0.03

From the results, it is obvious that the value of adsorption efficiency Q_m and adsorption energy b of the AGLS increases on increasing the temperature. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with endothermic nature of adsorption [14, 15]. To confirm the favorability of the adsorption process, the separation factor (R_L) was determined and are given in Table 4.The values established were found to be between 0 and 1 and there by confirm that the ongoing adsorption process is favorable [16].

Table 4. Thermodynamic parameter for the adsorption of mb onto AGLS

C₀	ΔG°				ΔH°	ΔS°
	30° C	40° C	50° C	60° C		
25	-7015.00	-7630.64	-8429.44	-8540.5	9.38	54.37
50	-5380.48	-5808.03	-7188.37	-7608.42	19.13	80.61
75	-4269.3	-4764.78	-5024.06	-5489.47	7.59	39.24
100	-2665.32	-3105.22	-5898.05	-3903.43	17.73	68.00
125	-1727.31	-2178.32	-4180.44	-3099.26	17.24	63.02

3.5.2 The Freundlich isotherm

The Freundlich isotherm model is the earliest known equation describing the adsorption process. It is an empirical equation and can be used for non-ideal sorption that involves heterogeneous adsorption. The Freundlich equation was employed for the adsorption of methylene blue dye on the adsorbent. The Freundlich isotherm was represented by the following equation.

$$\log Q_e = \log K_f + 1/n \log C_e \quad \text{.....................} \text{(2)}$$

Where Q_e is the amount of methylene blue dye adsorbed (mg/g), C_e is the equilibrium concentration of dye in solution (mg/L), and K_f and n are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of $\log Q_e$ versus $\log C_e$ shows that the adsorption of methylene blue obeys Freundlich adsorption isotherm. The values of K_f and n given in Table 4 shows that the increase of negative charges on the adsorbent surface makes electrostatic force like Vanderwaal's between the AGLS surface and dye ion. The molecular weight and size, either limit or increase the possibility of the adsorption of the dye onto adsorbent. However, the values clearly show the dominance in adsorption capacity.

The intensity of adsorption is an indication of the bond energies between dye and adsorbent, and the possibility of slight chemisorptions rather than physisorption [17, 18]. However, the multilayer adsorption of methylene blue through the percolation process may be possible. The values of n are less than one, indicating the physisorption is much more favorable [19].

4.6 Effect of temperature

To study the effect of temperature on the adsorption of dye adsorption by AGLS, the experiments were performed at temperatures of 30, 40, 50, 60°C. As it was observed that, the equilibrium adsorption capacity of MB onto AGLS was found to increase with increasing temperature, especially in higher equilibrium concentration, or lower adsorbent dose because of high driving force of adsorption. This fact indicates that the mobility of dye molecules increased with the temperature. The adsorbent shows the endothermic nature of

adsorption. The adsorption capacity of the AGLS increased with increase of the temperature in the system from 30° to 60°C. Thermodynamic parameters such as change in free energy ($\Delta G°$) (kJ/mol), enthalpy ($\Delta H°$) (kJ/mol) and entropy ($\Delta S°$) (J/K/mol) were determined using the following equations.

$$K_0 = C_{solid}/C_{liquid} \text{.....................} (3)$$
$$\Delta G° = -RT \ln K_O \text{.....................} (4)$$
$$\log K_0 = \Delta S°/ (2.303R) - \Delta H°/ (2.303RT) \text{.............} (5)$$

Where K_o is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant. The $\Delta H°$ and $\Delta S°$ values obtained from the slope and intercept of Van't Hoff plots are given in Table 5.The values of $\Delta H°$ are in the range of 9 to 17 kJ/mol. which indicate the physisorption. The results show that physisorption is much feasible for the adsorption of methylene blue. The positive values of $\Delta H°$ show the endothermic nature of adsorption which governs the possibility of physical adsorption [19, 20]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption increases and there is no possibility of chemisorption. The negative values of $\Delta G°$ (Table 5) show that the adsorption is highly favorable and spontaneous. The positive values of $\Delta S°$ (Table 5) show the increased disorder and randomness at the solid solution interface of methylene blue with AGLS adsorbent. The enhancement of adsorption capacity of the activated AGLS at higher temperatures was ascribed to the enlargement of pore size and activation of the adsorbent surface.

Table 5. The kinetic parameters for the adsorption of MB onto AGLS

C_0	Temp °C	PSEUDO SECOND ORDER				ELOVICH MODEL			INTRAPARTICLE DIFFUSION		
		q_e	k_2	γ	h	α	β	γ	K_{id}	γ	C
25	30	51.96	29×10^{-3}	0.996	7.91	64.98	0.13	0.9921	1.65	0.9912	0.18
	40	50.27	46×10^{-3}	0.993	11.83	1656.7	0.21	0.9924	1.78	0.9914	0.10
	50	50.93	44×10^{-3}	0.991	11.53	1383.8	0.20	0.9930	1.78	0.9915	0.10
	60	50.43	46×10^{-3}	0.9960	11.86	4751.2	0.23	0.9915	1.80	0.9917	0.09
50	30	97.30	17×10^{-3}	0.994	16.85	260.38	0.07	0.9940	1.67	0.9918	0.15
	40	97.13	23×10^{-3}	0.9955	22.21	1107.8	0.09	0.9923	1.73	0.9919	0.12
	50	100.1	20×10^{-3}	0.9952	20.47	1697.7	0.09	0.9928	1.75	0.9921	0.11
	60	99.30	22×10^{-3}	0.9953	22.30	3591.8	0.10	0.9927	1.77	0.9923	0.10
75	30	135.8	14×10^{-3}	0.9942	25.96	1134.4	0.06	0.9926	1.69	0.9925	0.12
	40	139.1	13×10^{-3}	0.9961	25.49	831.93	0.06	0.9933	1.68	0.9928	0.13
	50	138.3	15×10^{-3}	0.9956	28.84	2021.4	0.07	0.9935	1.72	0.9938	0.11
	60	140.6	14×10^{-3}	0.9974	28.64	1588.2	0.06	0.9936	1.71	0.9945	0.12
100	30	160.0	11×10^{-3}	0.9941	29.07	874.81	0.05	0.9939	1.62	0.9961	0.13
	40	166.4	10×10^{-3}	0.9944	29.11	683.98	0.05	0.9940	1.62	0.9967	0.14
	50	168.1	11×10^{-3}	0.9922	31.21	951.56	0.05	0.9941	1.64	0.9969	0.13
	60	172.9	10×10^{-3}	0.9932	31.38	1046.2	0.05	0.9943	1.65	0.9968	0.13
125	30	175.2	12×10^{-3}	0.9973	39.39	5003.1	0.06	0.9937	1.62	0.9977	0.10
	40	188.1	9×10^{-4}	0.9935	33.28	914.40	0.04	0.9928	1.58	0.9975	0.13
	50	194.2	9×10^{-4}	0.9936	33.94	867.17	0.04	0.9920	1.59	0.9974	0.14
	60	203.8	8×10^{-4}	0.9939	34.47	922.38	0.04	0.9919	1.62	0.9978	0.14

3.7. Adsorption kinetics
The study of adsorption dynamics describes the solute up take rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface .The kinetics of MB dye adsorption on to AGLS were analyzed using pseudo second-order[21] Elovich [22] and intra-particle diffusion[23] kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation co- efficient (γ) and the values are close or equal to 1. A relatively high correlation coefficient (γ) value indicates that the pseudo second-order model successfully describes the kinetics of MB dye adsorption.

3.7.1 The pseudo second- order equation
The pseudo second-order adsorption kinetic rate equation is expressed as
$$dq_t/d_t = k_2(q_e-q_t)^2 \text{.............}(6)$$
Where: k_2 is the rate constant of pseudo second- order adsorption (g mg/min). For the boundary conditions t = 0 to t= t and q_t = 0 to $q_t = q_t$ the integrated form of Eq. (6) becomes:
$$1/(q_e – q_t) = 1/q_e + K_2t \text{.................} (7)$$

This is the integrated rate law for a pseudo second-order reaction. Equation (7) can be rearranged to obtain Eq.(8),which has a linear form:

$$t/q_t = (1/k_2 q_e^2) + ((1/q_e)t \quad ……………..(8)$$

If the initial adsorption rate (h)(mg g^{-1}min^{-1}) is :

$$h = k_2 q_e^2 \quad ………………………………… (9)$$

Equation (8) and (9) becomes,

$$t / q_t = 1 / h + 1 / q_e \, t \quad ……………... …(10)$$

The plot of (t/q_t) and t of Eq. (10) should give a linear relationship and from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The pseudo-second order rate constants K_2, the calculated h values, and the correlation coefficients (γ) are summarized in Table 5.At all studied initial MB dye concentrations, the straight lines with extremely high correlation co-efficient (>0.99) were obtained. From Table 5, it is evident that the values of the rate constant k decreases with the increase initial MB dye concentration for AGLS. This shows that the sorption of MB dye on AGLS follows pseudo second order kinetic model [24, 25].

3.7.2 The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t / d_t = \alpha \exp (-\beta q_t) \quad ……..(11)$$

Where, α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation [22]. assumed $\alpha\beta t \gg t$ and by applying boundary conditions $q_t = 0$ at t= 0 and $q_t = q_t$ at t = t Eq.(11) becomes:

$$q_t = 1/\beta \ln (\alpha\beta) + 1/\beta \ln t \quad …………… (12)$$

If MB dye adsorption fits with the Elovich model, a plot of q_t vs. ln(t) should yield a linear relationship with a slope of $(1/\beta)$and an intercept of $(1/\beta)\ln (\alpha\beta)$. The Elovich model parameters α, β, and correlation coefficient (γ) are summarized in Table 5. The experimental data such as the initial adsorption rate (α) adsorption constant (β) and the correlation co-efficient (γ) calculated from this model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second–order kinetics models. This may be due to increase in the number of pores or active sites on the AGLS adsorbent.

3.7.3 The intra particle diffusion model

The intra-particle diffusion model used here refers to the theory proposed by Weber and Morris [23] based on the following equation for the rate constant:

$$q_t = k_{id} \, t^{(1/2)} + C ………………(13)$$

Where k_{id} is the intra-particle diffusion rate constant (mg/g/min) and C is the constant. If the rate limiting step is intra-particle diffusion, then the graph drawn between (q_t) (mg/g) verses square root of the contact time ($t^{1/2}$) should yield a straight line passing through the origin [23]. The slope of the graph will give the value of the intra-particle diffusion coefficient (k_{id}) and correlation coefficient (γ). The value of C gives an idea about the thickness of the boundary layer. From these data, the intercept value indicates that the line were not passing through origin, there are some other process affect the adsorption. But the correlation coefficient (γ) value is very high, so that the intra-particle diffusion takes place along with other process that may affect the adsorption. The values are given in **Table 5.**

3.7.4 Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. If the adsorbed dye can be desorbed using neutral pH water, then the attachment of the dye molecule of the adsorbent is by weak bonds. The effect of various reagents used for desorption studied. The results indicate that hydrochloric acid is a better reagent for desorption, because more than 90% removal of adsorbed dye was noticed with hydrochloric acid. The reversibility of adsorbed dye in mineral acid is in agreement with the pH dependent results obtained. The desorption of dye molecules by mineral acids and alkaline medium indicates that the dye was adsorbed onto the AGLS through physisorption as well as by chemisorption mechanisms.

IV. Conclusion

The present study has shown the effectiveness of using AGLS in the removal of methylene blue dye from aqueous solutions. Acid Activated Glossocardia linearifolia Stem in different forms has a great role in modern life to clean environment. Glossocardia linearifolia Stem can be a good precursors for producing highly porous AGLS carbon by simple preparative methods. An adsorption test has been carried out for industrial pollutants methylene blue under different experimental conditions in batch mode. The adsorption of methylene blue was dependent on adsorbent surface characteristics, adsorbent dose, methylene blue concentration, time of

contact and temperature. A study of the kinetic models on sorption showed that sorption fitted with the pseudo second- order kinetics model. The ΔG^0, ΔH^0, and ΔS^0 reveals the favorability of adsorption. The thermodynamic parameters suggested that the adsorption on AGLS was a spontaneous and endothermic process.

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